Measurements of ultrafast scintillation rise times: evidence of energy transfer mechanisms

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Abstract

The physical processes associated with scintillation growth and decay are investigated using ultrafast measurements of luminescence following pulsed X-ray excitation. Rise times with a time resolution of ~ 30 ps have been measured for several intrinsic and activated crystalline and amorphous materials at room temperature. Rise times of excitonic emission from CsI, CaF_2, Y_2SiO_5, $Y_3Al_5O_{12}$, $Bi_4Ge_3O_{12}$, CeF_3, and fused silica were less than our system response time, thus demonstrating very fast (< 30 ps) exciton formation. Rapid rise times of < 100 ps were observed for $CdS:Te^{2-}$, $CaF_2:Eu^{2+}$, and Ce^{3+}-activated aluminate, borate, phosphate, and borate crystals and silica and silicate glasses and are characteristic of prompt capture of holes at the activator site followed by electron capture. (Some Ce^{3+}-activated materials also exhibit a slower rise-time component(s) due to exciton-cerium transfer.) In contrast, CsI(Tl), CsI(Na), and NaI(Tl) have scintillation rise times of > 10 ns indicating excitation by prompt capture of electrons at the activator site followed by the known slower migration and capture of holes (V_k centers). Measurements of core-valence luminescence from BaF_2 and intraband luminescence from CsI are also reported. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

We have studied the scintillation growth and decay of intrinsic and activated oxide, halide, and chalcogenide materials using a pulsed X-ray system having a time resolution of ~ 30 ps. The various stages of the scintillation process [1] include the absorption of a high-energy photon creating an inner shell hole and an energetic primary electron, followed by radiative decay (secondary X-rays), nonradiative decay (Auger processes – secondary electrons), and inelastic electron–electron scattering in the time domain of 10^{-15}–10^{-13} s. When the electron energy becomes less than the ionization threshold, hot electrons and holes thermalize in $\sim 10^{-12}$–10^{-11} s by intraband transitions and electron–phonon relaxation; exciton formation, trapping of charge carriers on defects and impurities, and self-trapping also occur in this time interval. The luminescent centers may be excited by hot electron impact, sequential electron–hole capture or sequential hole–elec-

tron capture, and donor (exciton, sensitizer)–acceptor energy transfer processes in times ranging from $< 10^{-12}$ to $> 10^{-8}$ s. Therefore with the present experimental facility we are able to investigate a number of thermalization and excitation processes active in scintillators.

2. Experimental

The experimental configuration used is described in Ref. [2]. In the present experiments a frequency-doubled Ti:sapphire laser delivers 1-ps pulses of 400-nm light onto a light-excited X-ray tube to produce 90-ps pulses of X-rays at a rate of 0.8 MHz. The mean X-ray energy is ~ 20 keV, thus scintillation involving bulk rather than surface effects is dominant. A microchannel phototube with a bialkali photocathode and a response time of 35 ps fwhm was used to detect the scintillation photons in time bins of 3 ps. For wavelength selection, a filter or monochromator is inserted between the sample and detector. Single-crystal samples had dimensions ≤ 10 mm and were coated on five sides with dull black lacquer to

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absorb photons and thereby avoid an increased rise time due to multiple reflections. All measurements were made at room temperature. To determine the exponential rise and decay times, rise and decay components were convolved with the impulse response function of the system and the luminescent parameters varied to obtain a best chi-squared fit to the observed scintillation time dependence [2].

3. Core-valence and intraband luminescence

Core-valence luminescence (CVL) involves a transition wherein an electron in the valence band fills an hole in an inner shell with emission of a photon [1] and occurs in materials where the CVL photon energy is less than the band gap. The creation of the core hole is expected to occur in < 1 ps and thus is beyond our measurement capability. Therefore, the observed growth of the F 2p–Ba 5p transition CVL from BaF_2 shown in Fig. 1 is a measure of our system response.

Ultrafast luminescence attributed to hot carrier intraband radiative transitions has been reported for several materials. For CsI such luminescence was observed in the region 1.5–2.5 eV following excitation by a 50-ps electron pulse. Because an intraband radiative transition competes with electron–phonon relaxation, the decay time is fast, < 20 ps, and the quantum yield is very small, $\sim 2 \times 10^{-5}$ [3]. Using a 500-nm cut-on filter to absorb the CsI exciton emission centered at 315 nm, we observe a weak luminescence with a fwhm width of ~ 100 ps, again limited by our system response.

4. Exciton luminescence

Thermalized electrons and holes rapidly combine to form excitons. The formation time of self-trapped excitons in alkali halides measured with a pulsed electron beam was found to be ≤ 10 ps [4]. We have examined the rise time of excitonic emission from CsI, CaF_2, Y_2SiO_5, $Y_3Al_5O_{12}$, $Bi_4Ge_3O_{12}$, CeF_3, and fused silica. In all cases the rise times were < 30 ps and beyond our measurement limit. As an example, the luminescence from amorphous SiO_2 is included in Fig. 1.

5. Self-activated scintillators

$Bi_4Ge_3O_{12}$ And CeF_3 are examples of self-activated scintillators. The highest filled bands of these compounds correspond to the 6s and 4f states of Bi^{3+} and Ce^{3+}, respectively; the lowest unfilled bands correspond to the 6p and 5d states of these ions. Excited states are created by direct electron excitation and thermalization processes with resulting very fast (< 30 ps) rise times for the Bi^{3+} $6s6p(P_1) \rightarrow 6s^2(^1S_0)$ and Ce^{3+} $5d \rightarrow 4f$ transitions (see Fig. 1).

6. Activated scintillators: sequential hole–electron or electron–hole capture

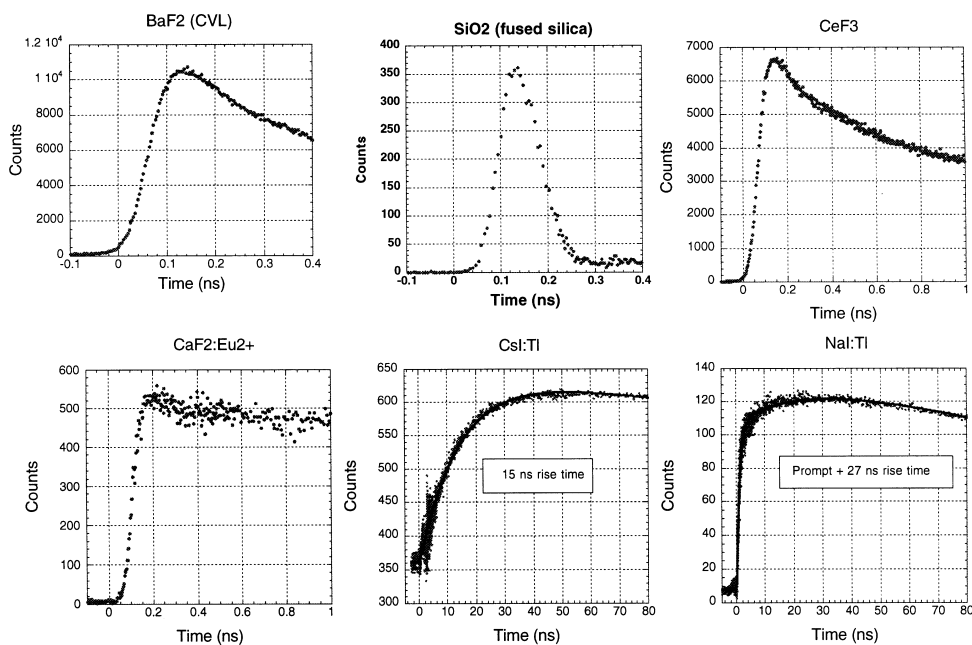Activated scintillators may be excited by (1) sequential hole–electron or (2) sequential electron–hole capture at

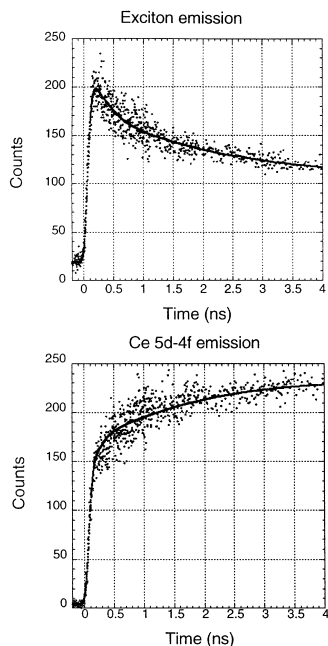Fig. 1. Examples of scintillation rise times measured at room temperature.

Fig. 2. Decay of exciton emission from $Y_3Al_5O_{12}$ (top) and growth of 5d–4f emission from $Y_3Al_5O_{12} : Ce^{3+}$ (bottom) due to sequential hole–electron capture and exciton energy transfer.

the activator site. (One does not want rapid efficient trapping of both electrons and holes by activators because this can lead to charge separation.) In the former case, an activator captures a valence band hole and then captures a conduction band electron to create an excited state of the activator or an activator-trapped exciton, following by emission of a scintillation photon. Materials with activators that are known to capture holes include $CdS : Te^{2-}$, $CaF_2 : Eu^{2+}$, and Ce^{3+} activated compounds. In these materials the observed rise times are very fast (see Figs. 1 and 2). The rise times in Ce^{3+}-activated glasses are also fast, but the scintillation efficiency is low because of the presence of traps and reduced mobility of electron and holes.

In the case of sequential electron–hole capture, if the hole self-traps this process requires that the lifetime of the activator-trapped electron be sufficiently long for the hole to migrate to the activator site. Examples of this behavior occur for CsI : Tl and CsI : Na (see Fig. 1). From the temperature dependence of the scintillation rise time, Valentine et al. [5] obtained an activation energy for hole (V_k center) migration. Excitonic emission from CsI activated with Cl, Br, and Pb does not show the slow rise time. V_k center migration is different in CsI and NaI. The time dependence of NaI : Tl scintillation shows a rise time behavior characteristic of prompt capture of nearby holes and delayed capture of migrating holes [6].

7. Donor-luminescent center transfer

If the host exciton emission overlaps absorption bands of the activator, resonant energy transfer can occur. We have observed this for many Ce^{3+}-activated scintillators. For example, the exciton emission of undoped $Y_3Al_5O_{12}$ centered at 310 nm has fast- and slow-decaying components and overlaps the 4f–5d absorption band of Ce^{3+} centered at 335 nm [7]. As shown in Fig. 2, the rise time of $Y_3Al_5O_{12} : Ce^{3+}$ has a prompt component characteristic of sequential hole–electron capture by Ce^{3+} and, in addition, slower rise time components due to exciton–Ce^{3+} transfer. We also observe a complex multicomponent sensitizer–activator rise-time behavior for $Gd_2SiO_5 : Ce$ arising from Gd^{3+}–Ce^{3+} energy transfer.

8. Conclusions

Measurements of scintillation rise times provide information about the rates of creation of core holes (CVL), creation of valence band holes (intraband luminescence), exciton formation, energy migration and transfer from electrons and holes created in an ionizing event to the luminescent center, and can be an indicator of whether an activator is an initial electron or hole trap. The results are also valuable in testing theoretical predictions of hole trapping and transport.

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